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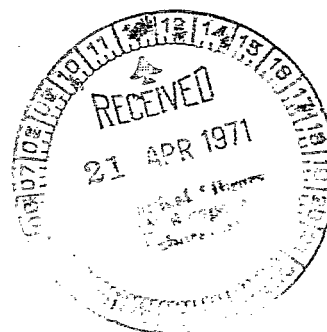


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INVESTIGATION OF FLAMELESS COMBUSTION MECHANISM OF M-2 DOUBLE-BASE PROPELLANT

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SUMMARY

An experimental study of the heat of reaction for the flameless combustion of M-2 double-base propellant (20 percent nitroglycerin, 77 percent nitrocellulose, 3 percent other ingredients) at pressures from 2.07 to 1380 kN/m² has been performed by use of differential scanning calorimetry and thermogravimetric analysis. The heat of reaction varied from 1.17 MJ/kg at 2.07 kN/m² to 3.02 MJ/kg at 1380 kN/m² with abrupt changes occurring near 13.8 kN/m², 138 kN/m², and 689 kN/m². The jumps in heat of reaction occurred at pressures corresponding to jumps in the burning rate and temperature jumps in the gas phase. These jumps are correlated to successive discrete gas-phase reactions which exist a few hundred micrometers above the deflagrating surface and these reaction zones move toward the surface as the ambient pressure is increased and intersect the surface at the same jump pressures.

On the basis of these results and the usual construction of a differential scanning calorimeter (DSC), it is concluded that the DSC is inadequate for measurements of the condensed-phase heat of reaction of double-base propellants, since the heat produced by these gas-phase reactions so close to the surface would also be detected by the instrument heat sensing system.

Comparison of differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) data shows that the desorption/vaporization of nitroglycerin occurs near the onset of significant heating and that no heating occurs before weight loss begins. This result implies that pure "condensed phase" contributions are minor for M-2 double-base propellant in the flameless combustion region.

INTRODUCTION

No reliable combustion model exists for the purpose of burning-rate tailoring of either double-base or composite solid propellants. Many comprehensive models have

*The material presented herein was included in a thesis entitled "Condensed Phase Reactions in M-2 Double-Base Propellants at Low Pressures" submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of South Carolina, Columbia, South Carolina, 1969.

been proposed (refs. 1, 2, and 3), but they cannot be applied conveniently because of the multitude of parameters that must be known or assumed. The controversy over the relative significance of condensed-phase and gas-phase reactions in the overall combustion process is still unresolved. Information on the low-pressure burning of double-base propellant is particularly scarce. The purpose of the investigation described herein is to determine the heat of reaction of M-2 double-base propellant (20 percent nitroglycerin, 77 percent nitrocellulose, and 3 percent other ingredients) in the low-pressure flameless regime and to determine, if possible, whether the reactions producing the heat were condensed phase, gas phase, or heterogeneous.

PREVIOUS INVESTIGATIONS

Heller and Gordon (ref. 1), using high-speed photography, observed that the combustion region of burning double-base propellants consists of three zones. (See fig. 1.) A "foam" zone, less than 1 mm in depth, in which the solid transforms to a viscous liquid and bubbles form, exists just below the surface. Above the burning surface is a large "dark" zone of supposedly nonreacting gases the length of which varies with pressure. As pressure increases, the flame gets closer to the surface. The third zone, which exists only at pressures greater than 689 to 1380 kN/m², depending on the particular propellant, is the "flame" zone. In the model of Parr and Crawford (ref. 2) and Rice and Ginell (ref. 3) also shown in figure 1, the "fizz" zone is introduced as an additional one between the foam zone and dark zone of the model of Heller and Gordon. This fizz zone exists even when there is no flame at low pressures.

Crawford, Huggett, and McBrady (ref. 4), using a closed bomb calorimeter pressurized with nitrogen and using low loading density of propellant, obtained some data on the overall heat of explosion for combustion. Their data are reproduced in figure 2. The propellant they used was 54 percent nitrocellulose, 43 percent nitroglycerin, and 3 percent ethyl centralite. It provided flameless combustion below 1.38 MN/m². They reported a heat of reaction of 2 MJ/kg for flameless combustion at this pressure. Analysis of the products of reaction also suggested to them that at low pressures, nitric oxide and other simple organic molecules react very close to the surface in the gas phase. More recent works (refs. 5 and 6) indicate that this is a very complex region.

In 1966 a translation of a journal article by Zenin (ref. 7) appeared. He used microthermocouples to determine temperature profiles in the condensed and gas phases and calculated corresponding heat release values, shown in figure 3. His results are of the same order of magnitude as the data of this paper and show a similar trend of decreasing heat release with pressure. The technique of analytically compensating for the heat-transfer contribution to the experimentally determined temperature profile is difficult to perform. This difficulty probably accounts for the large data scatter and

the failure to detect jumps in the heat of reaction. Failure to account for thermocouple lead losses, which can be significant as shown by Tsai (ref. 8), may also have caused some inaccuracies.

Waesche and Wenograd (refs. 9 and 10) have investigated condensed-phase reactions in composite ammonium perchlorate propellants. These authors claim that the combustion of composite propellants is strongly influenced by condensed-phase reactions. In reference 10 they cited flameless combustion, which sometimes occurs at low pressures, as evidence for condensed-phase reactions. However, as will be illustrated in this paper, a visible flame is not a requirement for gas-phase reactions to occur. Waesche (ref. 9) also states that the differential scanning calorimeter (DSC) is applicable to data acquisition for condensed-phase reactions "because the placement of the sensing elements in the base of the sample holders is such that only condensed-phase enthalpy changes are measured, and the gaseous reaction products are swept away by the steady purge stream." This statement is true only if there are no gas-phase reactions close to the burning surface.

Pliukhin (ref. 11) provided the basic equations used by Waesche and Wenograd in their studies. Pliukhin and several other authors that he refers to are the only ones who have investigated condensed-phase reactions in double-base propellants. Pliukhin indicates that they believe that nearly all the heat necessary for the flameless burning of double-base propellant is supplied by the condensed phase.

EXPERIMENT EQUIPMENT

Differential Scanning Calorimeter

The operation of the scanning calorimeter used in these experiments is based on the temperature control of two miniature sample holders in the assembly shown in figure 4. A block diagram of the system is shown in figure 5. The system consists of two separate control loops, one for average-temperature control, the second for differential-temperature control. In the average-temperature loop, a programmer provides an electrical signal which is proportional to the desired temperature of the sample and reference holders. The programmer temperature information is also relayed to the recorder-temperature marker pen and appears as the abscissa scale marking. The programmer signal is compared with the average signal from platinum resistance thermometers permanently embedded in the sample and reference holders. If the temperature required by the programmer is greater than the average temperature of the sample and reference holders, more power will be fed to the heaters of both sample holders. If the average temperature is greater than that required by the programmer, the power to both heaters



will be decreased. In this way, the average temperature of the holders is made to track the command from the programmer.

In the differential-temperature control loop, signals representing the sample and reference temperatures, measured with the platinum thermometers, are fed to a circuit which determines whether the reference or sample temperature is greater. The differential-temperature amplifier output will then proportion a small increment of power between the reference and sample heaters in such a way as to correct any temperature difference between them. A signal proportional to the differential power is also transmitted to the main recorder pen. The integral of the resulting peak is the internal energy change. The direction of the pen excursion will depend upon whether more power is required in the sample or reference heater.

Provision is made for removal of decomposition gases by allowing an inert gas to flow through the sample holder assembly. A diagram of the gas flow path is shown in figure 6. Examination of this figure shows that gaseous reactions which occur close to the surface cannot be swept away by the purge gas. The sample holder and its aluminum dome-shaped cover constitute an essentially closed system except for the small amount of purge gas which leaks in around the crack between the holder and cover against the outward flow of decomposition gases. A photograph of the assembled DSC and TGA system is shown in figure 7.

The DSC as available from the manufacturer was capable of measurements at and below atmospheric pressure. For the work reported in this paper, pressures above atmospheric were desired. An additional sample holder assembly with its mounting hardware was obtained from the manufacturer and was mounted in a spherical pressure vessel shown in the sketch in figure 8 and the photographs in figure 9. The vacuum and purge-gas connections and valve system for the high-pressure DSC and TGA system are sketched in figure 10. Electrical connections were tapped into the existing atmospheric-system electronics, and a switch was added to allow use of either sample holder assembly. However, to eliminate possible variations in the sample holders, the high-pressure vessel and its sample holder assembly were used for vacuum and high-pressure tests. The vacuum and purge-gas system was connected to the pressure vessel also. A continuous purge flow of 20 to 30 cm³/min, as measured with flowmeters, was maintained during all tests above and below atmospheric pressure. The pressure vessel was designed to handle 3450 kN/m². However, at pressure above 517 kN/m² preventing base-line drift was difficult probably because of the increase in thermal conductivity of the environmental inert gas, which was argon in this test. However, this drift represented a minor percentage of the quantitative results.

Thermogravimetric Analysis Equipment

The thermogravimetric analysis system provides a record of microgram-level weight changes in a sample as a function of temperature from ambient to 1000° C. It utilizes a Cahn RG electrobalance mounted in a glass vacuum chamber and thereby allows control of the atmosphere around the sample, which is suspended from the balance beam of the electrobalance into a furnace below. The electrobalance provides a sensitivity of 0.1 μ g. The furnace consists of a platinum resistance heating element wrapped around the outside of a ceramic cylinder 0.95 cm in diameter. The location of the furnace within the chamber permits close coupling of heat source and sample to allow rapid scanning without information loss. The furnace acts as a heater and as a temperature sensor. In the temperature sensing mode, it forms one side of a bridge circuit. The other side of the bridge circuit is driven by the output signal from the temperature programmer. An error signal proportional to the temperature error is developed and fed into an amplifier. In the heating mode, the amplifier output is connected to the heater by means of an electronic system which provides 60-hertz power pulses designed to correct the temperature error.

EXPERIMENTAL PROCEDURES

DSC Experimental Procedure

Two types of samples were used in the scanning-calorimeter experiments. The first type, used in the nitroglycerin detection tests, was cut from a rod of propellant approximately 3 mm in diameter. Disks of 0.6 to 0.7 mm thick were cut by use of lathe and knife-edge cutting tool. Weights ranged from 16 to 22 mg. Each disk was placed in the small aluminum pans provided with the scanning calorimeter and covered with a lid of aluminum which was pierced 10 times with a hypodermic needle 0.5 mm in diameter to allow gaseous decomposition products to escape. The edges of the pan were then crimped with a special tool provided with the calorimeter in order to enclose the sample disk of propellant. The sample pan was then placed in the sample holder assembly, and an empty sample pan was placed in the reference sample holder. (This procedure is acceptable in differential scanning calorimetry where the specific heat of the reference material does not have to be similar to the sample, as in differential thermal analysis.) The range selection switch was set at either 8 or 16 mJ/sec for full-scale deflection. These were the most sensitive settings of the instrument. The needle valve for controlling argon flow was then opened enough to allow for a purge flow rate of 20 to 30 cm³/min. For tests below atmospheric pressure, the vacuum pump was started and the bypass valve opened to maintain the desired pressure. The argon needle valve was then readjusted for a purge flow rate of 20 to 30 cm³/min. For tests above atmospheric pressure, the valve at the entrance to the pressure vessel was opened, and the pressure

regulator on the argon supply tank was set to the desired pressure. Simultaneous adjustment of the argon needle valve and the outlet valve in the vacuum line provided a purge flow through the same path as for low-pressure tests and at the same rate.

After waiting for the pressure and purge flow to stabilize, the temperature scan was initiated. The slope control was then adjusted to produce a vertical run along the center of the paper when no chemical reactions occurred. When exothermic reactions started in the sample, the recorder pen deviated from the center line. When full-scale position was reached, the test was stopped by cutting off the main power switch and argon supply tank valve. Measurements such as these were made at various pressures between 2.07 and 689 kN/m². Results of these tests are discussed subsequently.

The second method of sample preparation was required to prevent self-heating in tests for which the heat of reaction was measured. If self-heating of the sample due to exothermic reactions exceeds the amount required to maintain the programed heating rate, inaccurate results are obtained. Excessive self-heating was prevented by mixing 10 percent or less of finely powdered propellant with a material known to be chemically inert over the range of temperature and pressure being investigated. Polyphenyl ether (ref. 12), a liquid used as a high-temperature hydraulic fluid and as a high-vacuum lubricating oil, was a suitable material. The polyphenyl ether is viscous enough to hold the propellant particles in suspension for many hours; thus, the researcher can be confident of the homogeneity of the mixture.

A sample pan of pure polyphenyl ether was scanned over the temperature range of 25⁰ C to 350⁰ C at pressures as low as 1.3 kN/m² and was found to be stable and did not vaporize. A known amount of polyphenyl ether was placed on a glass microscope slide, and a preweighed amount of finely powdered propellant (10 percent or less) was mixed with the polyphenyl ether and stirred to form a slurry. A small droplet of slurry was then placed inside a 6-mm ring of 30-gage nickel wire and covered with a lid pierced 10 times with a hypodermic needle and crimped at the edges. The wire ring prevented the liquid from being squeezed out during the crimping process. The sample pan, ring, and lid were weighed before and after adding the slurry to determine the amount present in each sample pan accurate to 1/10 mg. Slurry weights of roughly 20 mg at 5 to 10 percent propellant produced curves which remained on scale for range settings of 33.5 to 67.0 mJ/sec, depending on the pressure. The procedure for setting pressure and purge flow was the same as that for disk samples. For these tests, the programed temperature rise rate was allowed to continue until exothermic reactions ceased and the marker pen returned to the base line. The base line sometimes drifted slightly in the exothermic or endothermic direction, depending on the accuracy of the adjustment of the slope control at the beginning of a test. Several tests at one pressure usually allowed a proper

setting to be achieved. Some readjustment was usually required when the pressure was changed between tests.

The heat-of-reaction tests usually produced a bell-shaped curve. The area under the curve, bounded by a base line drawn tangent to the lower edges of the bell, was measured with a mechanical planimeter. The planimeter was then used to measure the area of a rectangle which was one-half of the chart in width, and in length equaling 1 minute of test time. (For example, if the chart speed is 10.2 cm per minute, the rectangle is 10.2 cm long.) A direct measure of the heat of reaction in joules is then given by

$$\text{Heat of reaction} = \frac{(\text{Area of sample peak})(\text{Range setting})(60)}{(\text{Area of rectangle})}$$

This was then divided by the weight of propellant in the sample to obtain the heat of reaction in joules per kilogram.

One other procedure, with small amounts (less than 2 mg) of pure powdered M-2 propellant, was tried. The resulting curves remained on scale for range settings of 134 mJ/sec. These samples also must be enclosed in sample pans with pierced lids to prevent ejection of powder fragments from the sample pan due to purge-gas flow or decomposition-gas flow, causing spurious peaks on the recorder.

TGA Experimental Procedure

Procedures were based on the TGA operator's manual provided by the manufacturer. A prime objective in sample preparation was to maintain the best possible thermal contact with the sample pan in order to give sharp and reproducible results. Sample sizes which fell in the optimized range of the instrument of 0.5 to 10 mg were used. The tests at 10⁰ C per minute used samples of 7 to 8 mg, which had been cut from the same rods of propellant used for the DSC sample disks. Thicknesses of about 0.25 mm provided as much surface contact with the sample as possible. Aluminum sample pans, approximately the same size as DSC sample pans, were first used but could be used only once. The carbonaceous residue, which remained after a run in which complete deflagration occurred, was difficult to remove without bending or damaging the soft thin pans. Platinum sample pans were found to be more suitable for reuse, since they could be easily cleaned by scraping with a small screwdriver point and washing with acetone.

A sample of the desired size, determined by preweighing on an analytical balance accurate to 1/10 mg, was placed in the sample pan as in the DSC experiment, except no lid was used. A lid is required in the TGA only when sputtering of the sample may occur, causing some of the sample to fall from the pan. The range was so that a 1-mg

weight loss would cause a full-scale recorder deflection. A recorder chart speed proportional to the temperature scan speed which will provide a trace without extremely small or extremely large slopes for ease of data interpretation was selected. The scan rate was selected and the switch turned on to start the heating program.

EXPERIMENTAL RESULTS

Vaporization of Nitroglycerin From Propellant

In maximum sensitivity tests with the 20-mg disk samples in the DSC, the first recognizable departure from the base line occurred at approximately 140° C for a heating rate of 10° C per minute. This exothermic indication continued to increase gradually as shown in figure 11. At approximately 165° C, the established trend in the exothermic direction dipped slightly and then resumed its increase. This dip appears to be an endotherm on top of the established exothermic rate. If the main power switch was cut off prior to 165° C, the propellant sample holder was found to be clean. But, if the temperature was allowed to increase beyond this point, a small amount of brown oily residue was found on the under side of the aluminum dome-shaped cover over the sample holder cup and around the outside of the sample holder cup. This phenomenon consistently occurred at 165° C for all pressures from 2.07 to 689 kN/m² at a heating rate of 10° C per minute. At this same temperature and heating rate, TGA results (which will be discussed in detail subsequently) indicated a sudden increase in the rate of weight loss and thereby supported the idea of desorption/vaporization at this point.

To perform an infrared analysis, a sample of this brown oily liquid was collected by making repeated tests without cleaning the sample holder assembly. An infrared spectrum of this liquid indicated that it was primarily nitroglycerin, as shown by comparing figures 12 and 13 (ref. 13). The appearance of this brown oily liquid at low pressures had been noticed by Suh and Clary (ref. 14) and by Crawford, Huggett, and McBrady (ref. 4), who thought it was glyoxal. However, the infrared spectrum of glyoxal, shown in figure 14 (ref. 15) does not match that of figure 12. Also, glyoxal is fluorescent under ultraviolet light, but a sample of the brown oily liquid, when exposed to ultraviolet light, did not fluoresce. Apparently, glyoxal is either absent or present only in small quantities.

Variation of Heat of Reaction With Pressure

Typical recorder outputs for the heat of reaction tests are shown in figure 15. The heat of reaction varied with pressure as shown in figure 16. Jumps in exothermic heat of reaction occurred between 6.89 and 13.8 kN/m², 101 and 207 kN/m², and again between 760 and 1520 kN/m².

The results of tests with pure propellant powder are shown by \square in figure 16. Possible self-heating effects and the difficulty of controlling heat input and distribution in the powder, as opposed to the powder in polyphenyl ether, probably made the powder results less precise. They are included to show essential agreement with polyphenyl ether results. Thus, any reaction between the propellant and/or its products of decomposition with the polyphenyl ether, if it occurred at all, was very minor.

These jump phenomena agree with the results of Suh and Clary (ref. 14) shown in figure 17 and the results of Thompson (ref. 16) shown in figure 18. The curves in figure 17 were parallel from 16.5 to 101 kN/m² with a change in slope between 101 and 448 kN/m². From 448 to 793 kN/m², the curves were again roughly parallel, and another change in slope appeared between 793 and 1138 kN/m². The data of Thompson (ref. 16) indicate that temperature jumps occur very close to the surface and move toward the surface as pressure increases. The pressures at which these jumps in temperature reach the surface agree approximately with the jumps in heat of reaction and the change in slope of the curves of burning rate as a function of initial temperature. The abrupt changes in burning rate seemed to occur over a wide range of initial temperatures and appeared to be more pronounced at higher initial temperatures, as indicated by the divergence of the curves in the jump regions at higher initial temperatures, as shown in figure 17.

The geometric environment of the propellant powder in polyphenyl ether is obviously different from that which exists in a burning slab of solid propellant. However, bubbles which are observed in the viscous foam zone due to gas-producing reactions are small enough to originate on pieces of powder. Bubbles can also occur in the polyphenyl ether. Apparently the surface areas within these bubbles are not too different to prevent gas-phase and/or heterogeneous reactions from occurring, since the jump phenomenon was detected for both types of environment. The interaction of propellant powder with polyphenyl powder may affect the quantitative results slightly but not the qualitative results.

Nitroglycerin Detection By TGA

With an approximately 8-mg propellant sample at a scan speed of 10° C per minute, the first detectable weight loss began at approximately 90° C. The first detectable weight loss always occurred at temperatures lower than the first detectable heat generation. The weight loss increased slightly with temperature, as shown by the representative curve in figure 19, up to 165° C where a sudden increase in rate of weight loss occurred. This increase in weight-loss rate, which occurred at the same point for all pressures of the tests, coincided with the endothermic anomaly from the scanning-calorimeter results. This change in slope indicated a possible desorption/vaporization or at least a new type

of reaction associated with the desorption/vaporization of nitroglycerin. The fact that the temperature at which this increase occurred did not change with pressure for any of the pressures of the test (6.65 kN/m² to atmospheric pressure) is an indication that the nitroglycerin does not act independently as an ingredient when it is mixed in the propellant.

After the "knee" was reached, the weight-loss rate increased very rapidly, and rapid deflagration of the sample resulted. Cutting off the main power switch after the knee did not prevent complete deflagration from occurring, as could be done with the scanning calorimeter. Evidently, the larger thermal mass of the TGA heating system kept the temperature up long enough for runaway conditions to occur; whereas the low thermal mass of the scanning calorimeter cooled rapidly enough to prevent it.

CONCLUDING REMARKS

The heat of reaction of a double-base propellant has been measured by use of a differential scanning calorimeter and found to vary with pressure in the flameless combustion regime from approximately 689 kN/m² to 2.07 kN/m². However, the variation was not continuous. Abrupt changes occurred in the 13.8 kN/m² and 138 kN/m² regions in the flameless regime. Another abrupt change, which was accompanied by a visible flame, was detected near 689 kN/m². The fact that no visible flame occurred was not a justification for ruling out gas-phase reaction as has been claimed by others. These reactions occur very close to the surface and are therefore measured with a differential scanning calorimeter. This instrument is therefore incapable of distinguishing condensed-phase reactions from gas-phase or heterogeneous reactions which may occur close to the surface.

The fact that weight loss, as indicated by thermogravimetric analysis measurements, always began before heat generation implies that gaseous decomposition products or reaction products were evolved in the heat-producing reactions. The heat of reaction also continued to vary at all pressures down to the limit of the equipment used (2.07 kN/m²).

Comparison of measurements from thermogravimetric analysis and differential scanning calorimeter indicated that desorption/vaporization of nitroglycerin occurred prior to the beginning of significant heat generation. These facts, coupled with the burning rate and temperature profiles of C. L. Thompson (Ph. D. Dissertation, University of South Carolina, 1968) and the initial temperature studies of Suh and Clary (AIAA Journal, vol. 8, no. 4, 1970), imply that the heat necessary for flameless

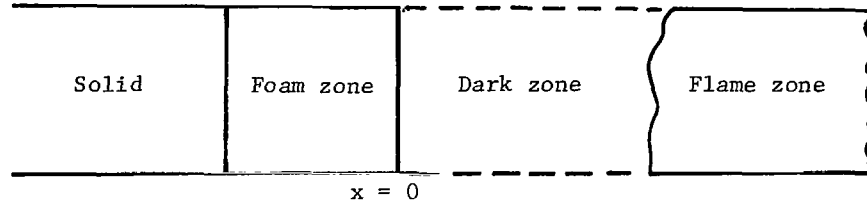
combustion may not be supplied entirely by the condensed phase as has been indicated by Zenin (Combustion, Explosion, and Shock Waves, vol. 2, no. 1, 1966).

Langley Research Center,
National Aeronautics and Space Administration,
Hampton, Virginia, February 2, 1971.

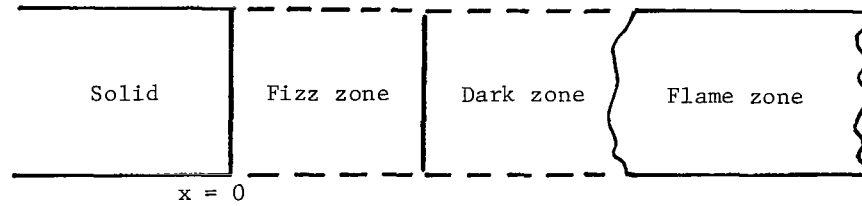
REFERENCES

1. Heller, C. A.; and Gordon, Alvin S.: Structure of the Gas Phase Combustion Region of a Solid Double Base Propellant. J. Phys. Colloid Chem., vol. 59, no. 8, Aug. 1955, pp. 773-777.
2. Parr, Robert G.; and Crawford, Bryce L., Jr.: A Physical Theory of Burning of Double-Base Rocket Propellants. I. J. Phys. Colloid Chem., vol. 54, no. 6, June 1950, pp. 929-954.
3. Rice, O. K.; and Ginell, Robert: The Theory of the Burning of Double-Base Rocket Powders. J. Phys. Colloid Chem., vol. 54, no. 6, June 1950, pp. 885-917.
4. Crawford, Bryce L., Jr.; Huggett, Clayton; and McBrady, J. J.: The Mechanism of the Burning of Double-Base Propellants. J. Phys. Colloid Chem., vol. 54, no. 6, June 1950, pp. 854-862.
5. Dauerman, L.; Salser, G. E.; and Tajima, Y. A.: Evidence for Nitrogen Trioxide in the Combustion of a Double-Base Propellant. J. Phys. Chem., vol. 69, no. 10, Oct. 1965, pp. 3668-3669.
6. Phillips, L.: Comment on "Evidence for Nitrogen Trioxide in the Combustion of a Double-Base Propellant." J. Phys. Chem., vol. 72, no. 6, June 1968, p. 2279.
7. Zenin, A. A.: Burning of Nitroglycerin Powder in Vacuum and at Subatmospheric Pressures. Combust. Explos. Shock Waves, vol. 2, no. 1, Spring 1966, pp. 42-44.
8. Tsai, C. L.: The Surface Temperature of M-2 Double Base Propellants at Low Pressures. M. S. Thesis, Univ. of South Carolina.
9. Waesche, R. H. Woodward: Research Investigation of the Decomposition of Composite Solid Propellants. Rep. H910476-36, United Aircraft Corp., Sept. 1969.
10. Waesche, R. H. W.; and Wenograd, J.: Calculation of Solid Propellant Burning Rates From Condensed-Phase Decomposition Kinetics. AIAA Paper No. 69-145, Jan. 1969.
11. Pliukhin, B. I.: On the Stationary Theory for Heat Balance of Powder and Explosive Condensed Phases. Eighth Symposium (International) on Combustion, Williams & Wilkins Co., 1962, pp. 734-745.
12. Wilson, Donnell R.; Marshall, William A.; Dolle, Roland E.; and Benzing, Robert J.: Physical, Chemical, and Mechanical Characteristics of a Polyphenyl Ether. Ind. Eng. Chem. Prod. Res. Develop., vol. 6, no. 2, June 1967, pp. 81-88.
13. Pristera, Frank; Halik, Michael; Castelli, Alexander; and Fredericks, Walter: Analysis of Explosives Using Infrared Spectroscopy. Anal. Chem., vol. 32, no. 4, Apr. 1960, pp. 495-508.

14. Suh, N. P.; and Clary, D. L.: Steady-State Burning of Double-Base Propellants at Low Pressures. AIAA J., vol. 8, no. 4, Apr. 1970, pp. 825-827.
15. Harris, R. K.: Vibrational Assignments for Glyoxal, Acrolein and Butadiene. Spectrochim. Acta, vol. 20, no. 7, July 1964, pp. 1129-1141.
16. Thompson, C. L., Jr.: An Investigation Into the Mechanisms of Combustion of a Double-Base Solid Propellant. Ph. D. Thesis, Univ. of South Carolina, Aug. 1969.



(a) Model of Heller and Gordon (ref. 1).



(b) Model of Rice and Ginell (ref. 3).

Figure 1.- Double-base combustion models.

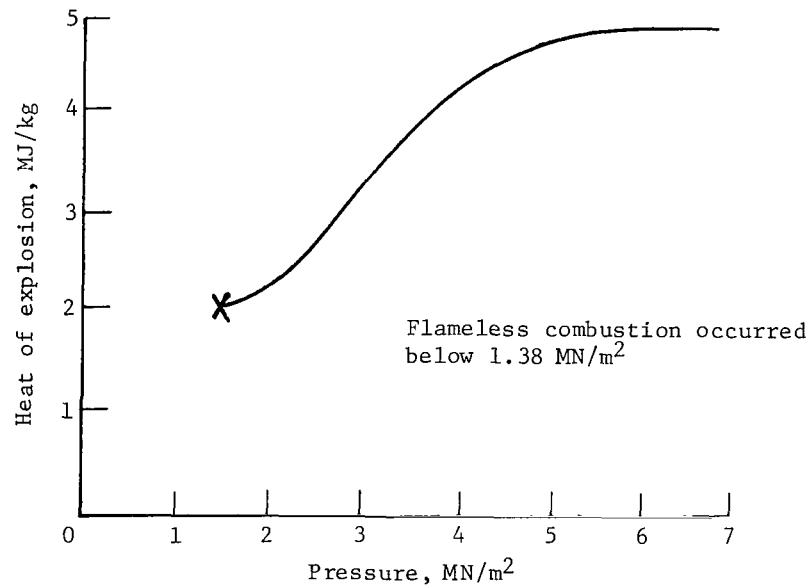


Figure 2.- Variation of heat of explosion with pressure (ref. 4).

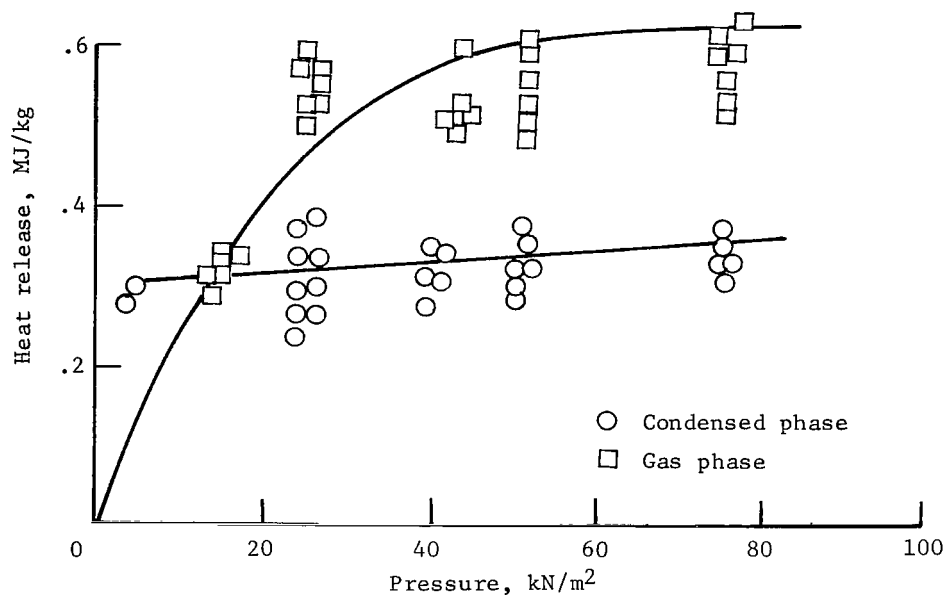
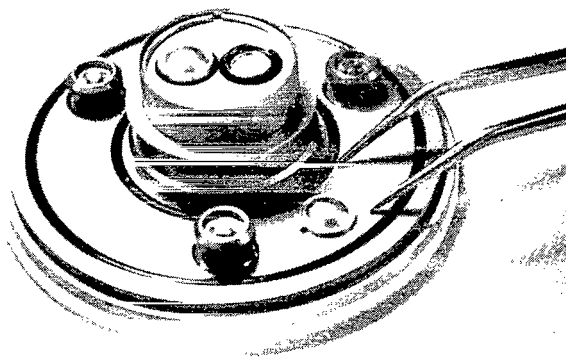


Figure 3.- Heat release per kilogram of propellant (ref. 7).



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Figure 4.- DSC sample holder assembly.

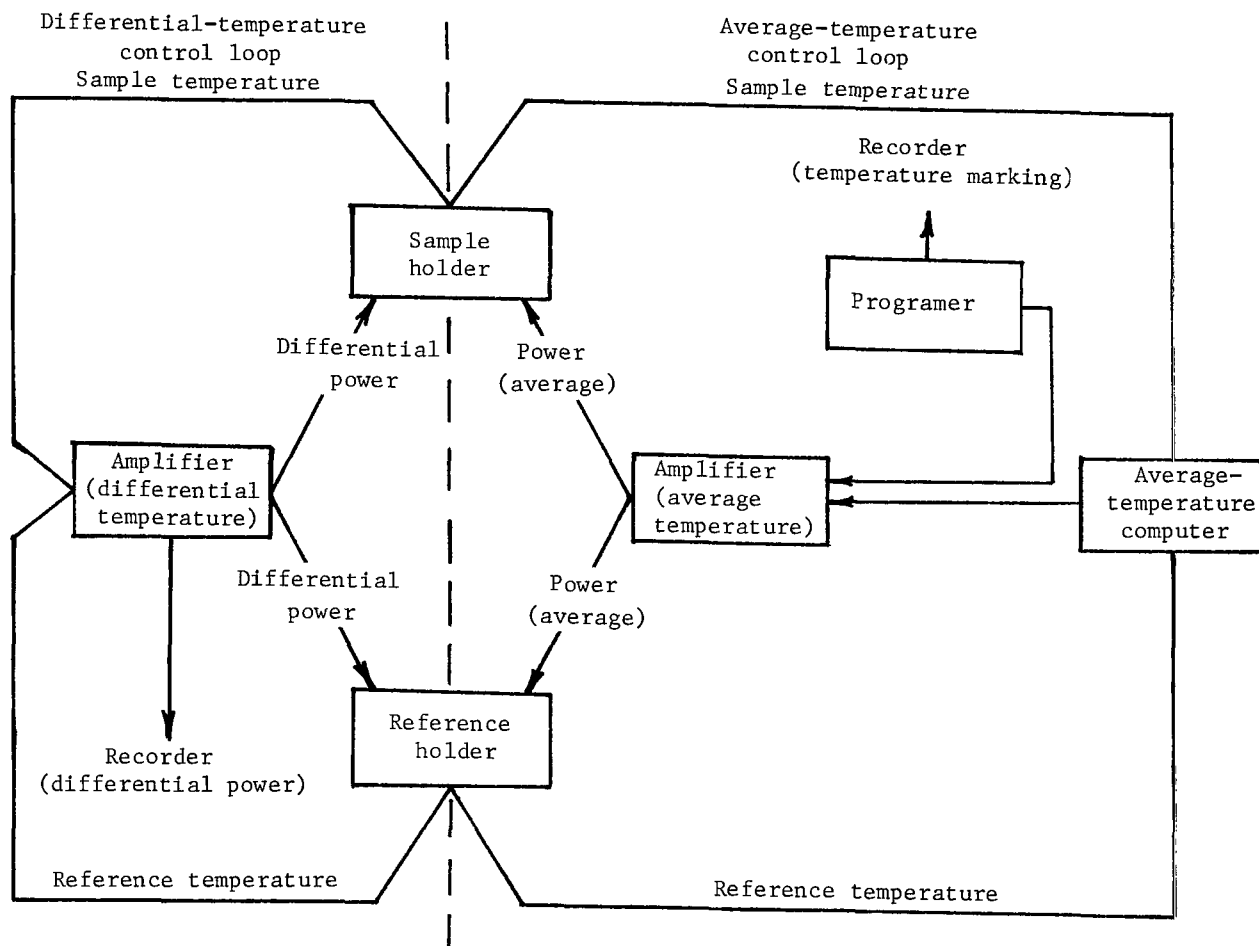


Figure 5.- DSC block diagram.

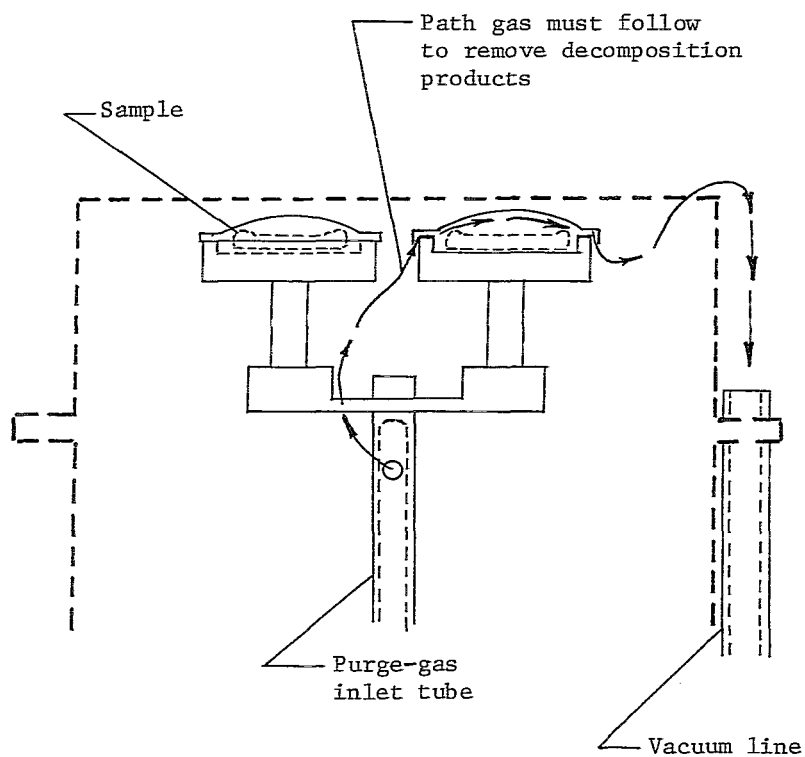
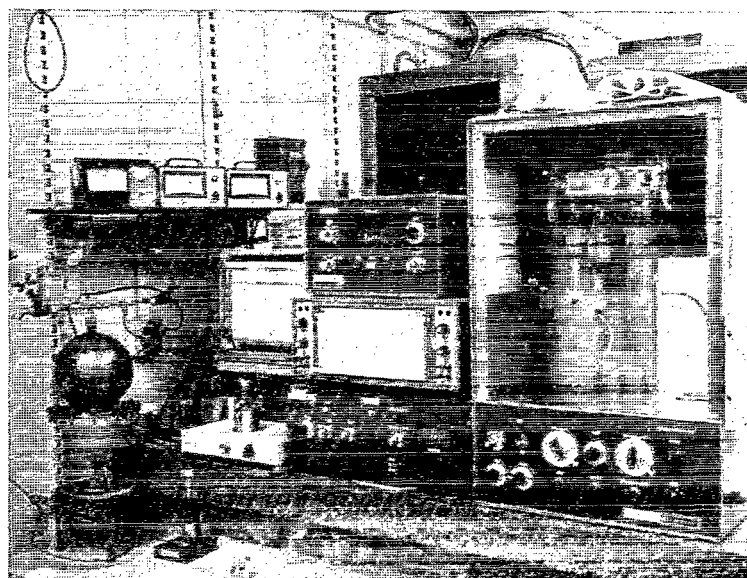


Figure 6.- Diagram of DSC purge-gas flow path.



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Figure 7.- DSC and TGA system.

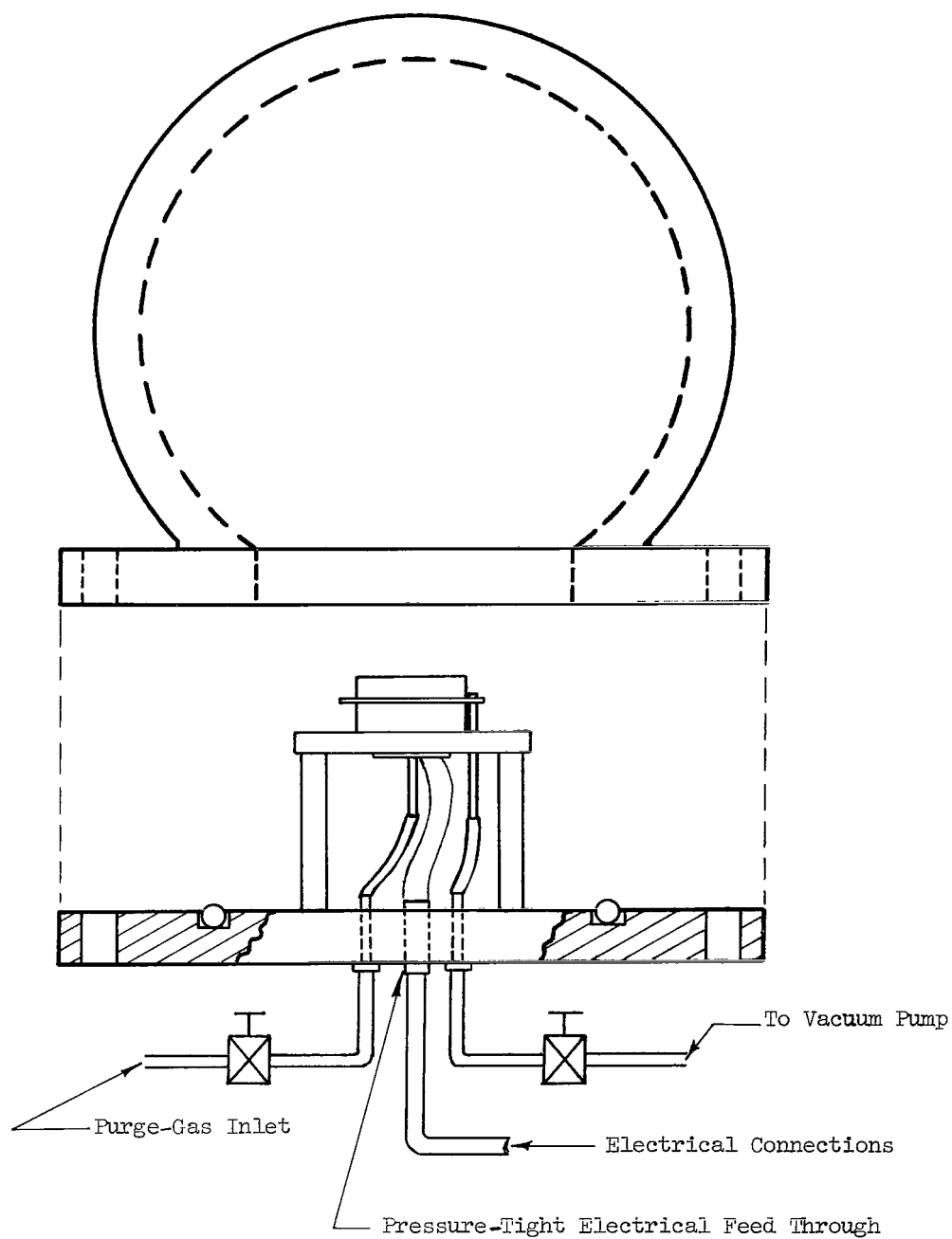
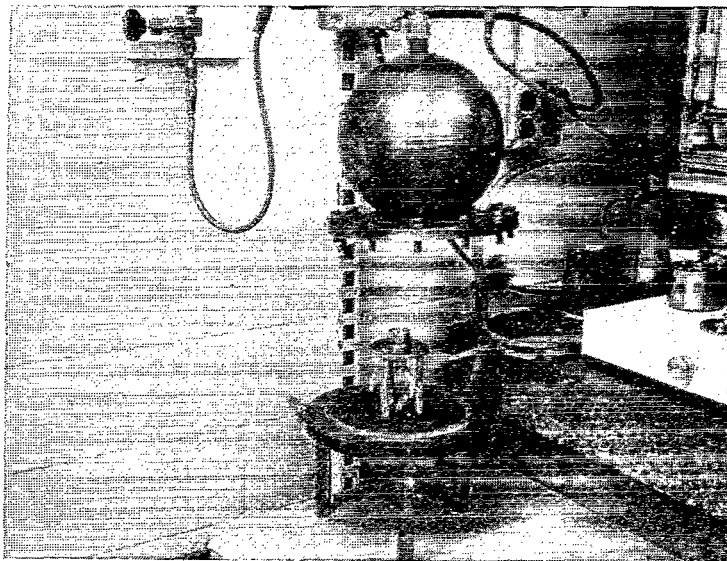


Figure 8.- Sketch of DSC pressure vessel and sample holder.



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Figure 9.- Photographs of DSC pressure vessel
and sample holder.

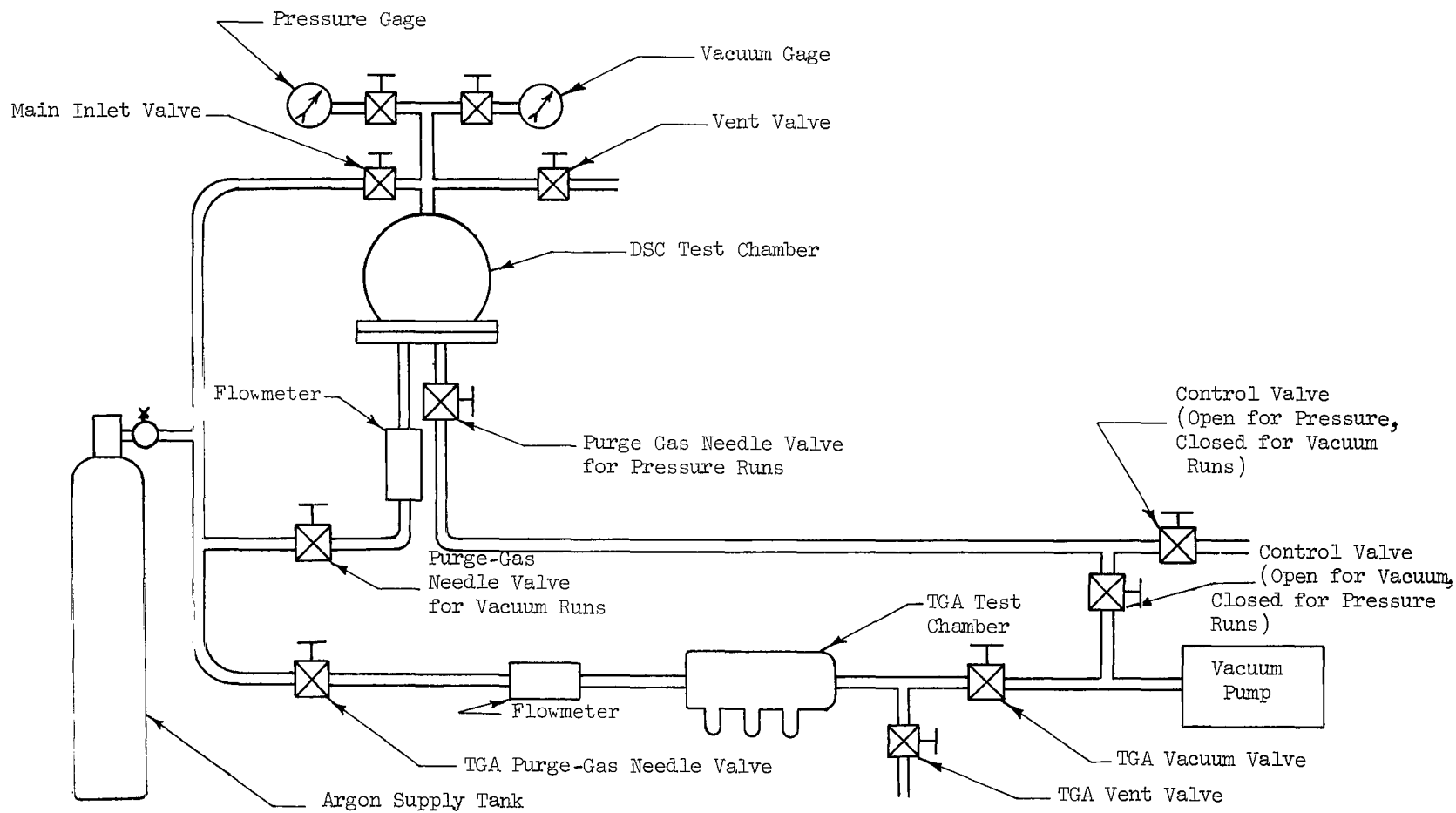


Figure 10.- DSC and TGA vacuum and purge-gas system.

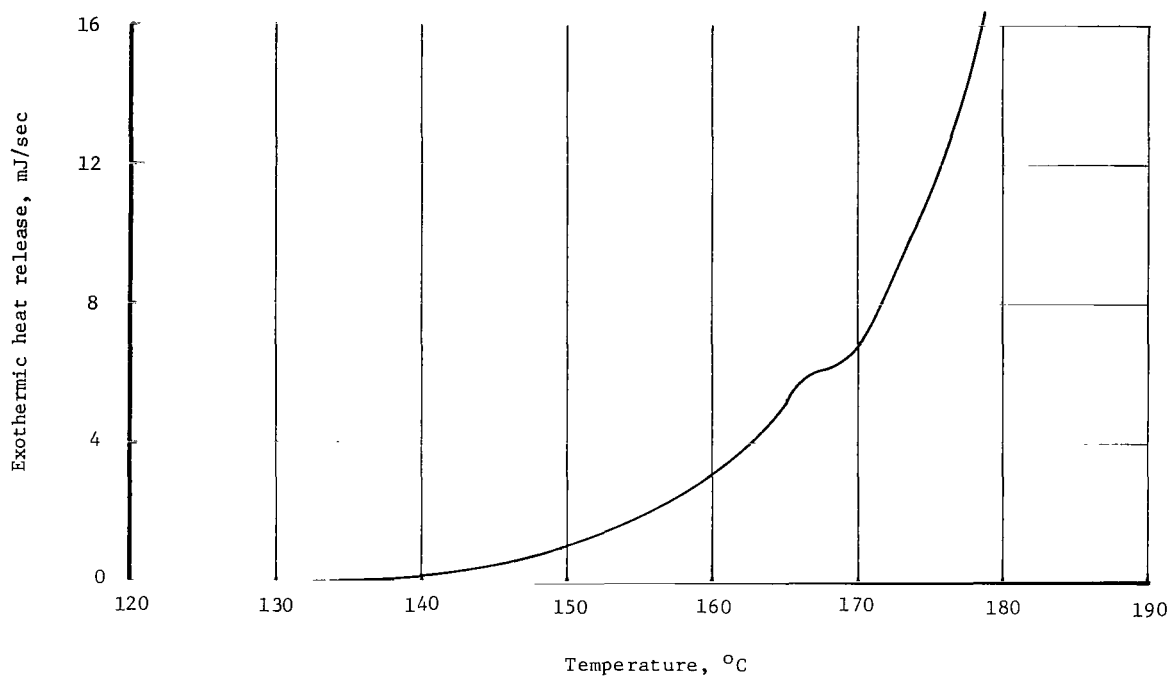


Figure 11.- DSC endothermic anomaly for disk of M-2 propellant.
20-mg disk sample; Range = 4; heating rate of 10° C per minute.

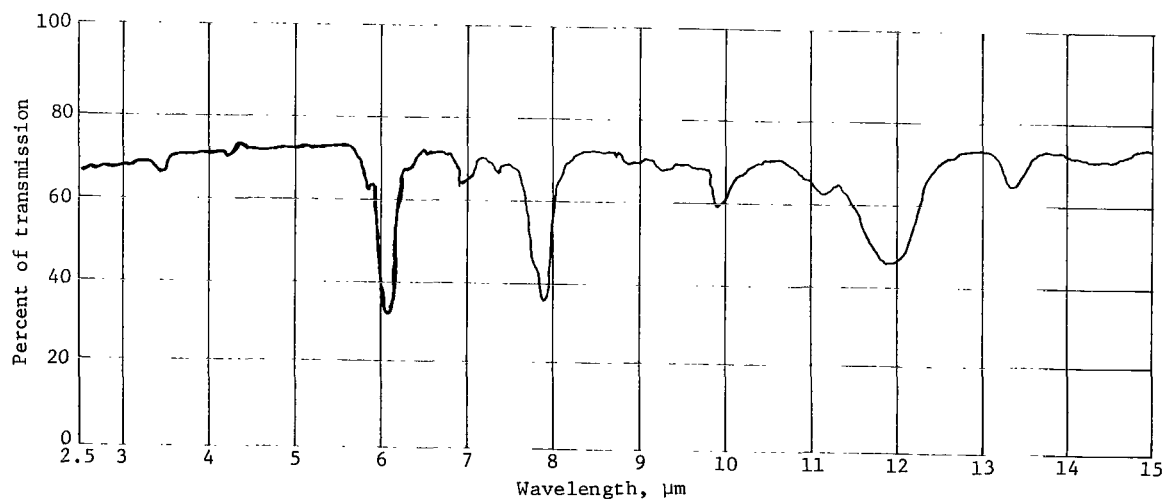


Figure 12.- Infrared spectrum of oily liquid.

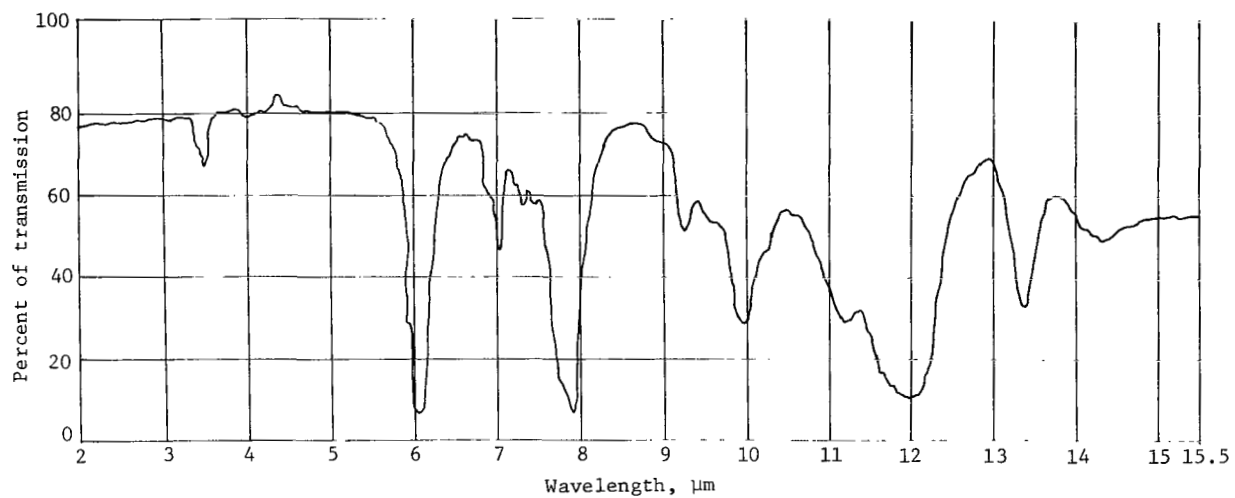


Figure 13.- Infrared spectrum of nitroglycerin (ref. 13).

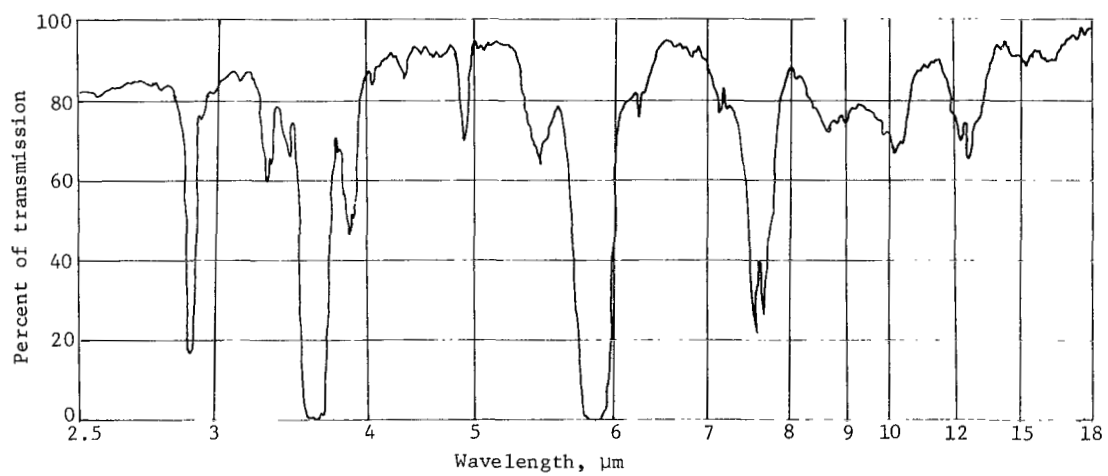


Figure 14.- Infrared spectrum of glyoxal (ref. 15).

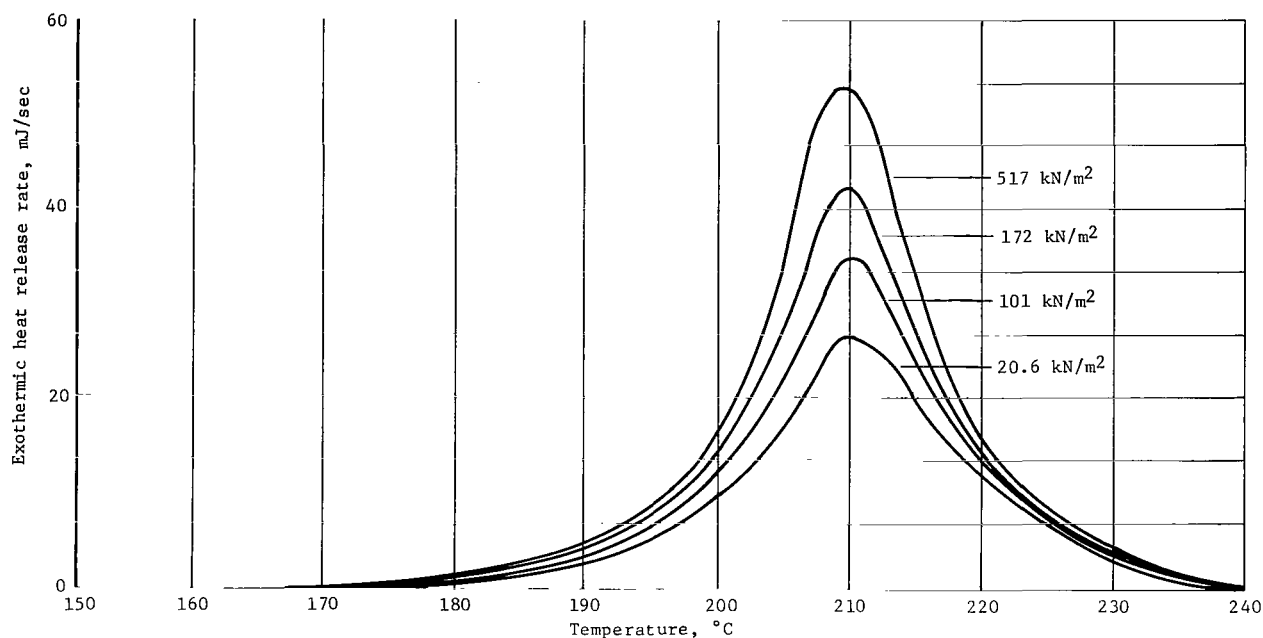


Figure 15.- Variation of heat release rate with pressure.
1 mg of M-2 powder in 9 mg of polyphenyl ether.

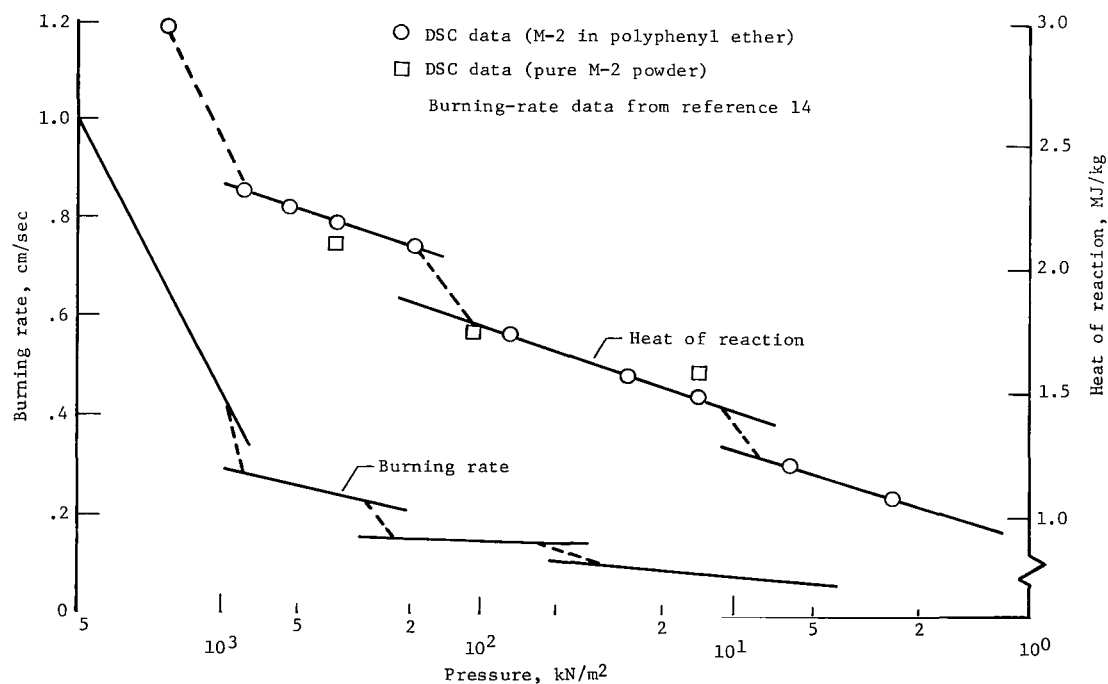


Figure 16.- Variation of heat of reaction and burning rate with pressure.

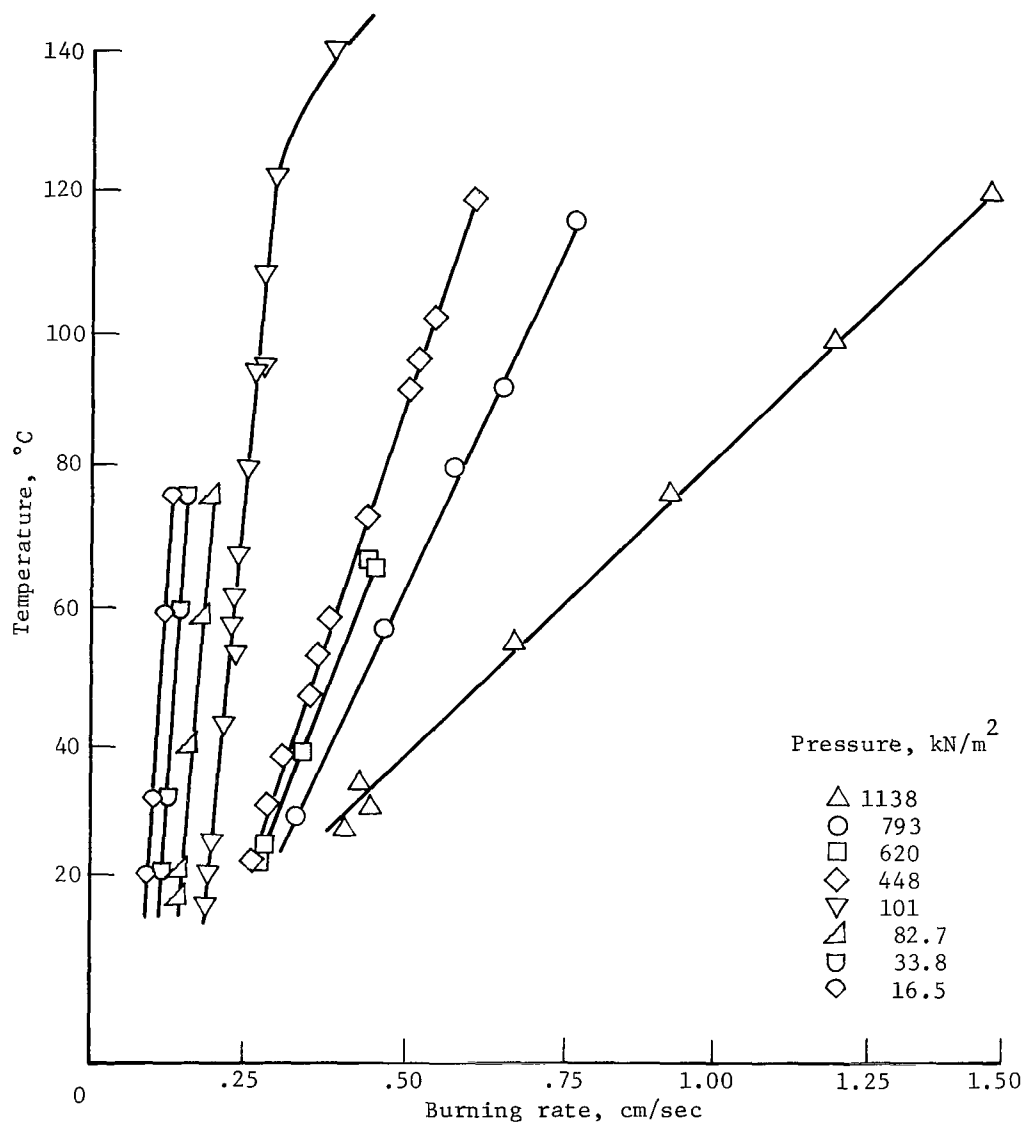


Figure 17.- Variation of burning rate with initial temperature (ref. 14).

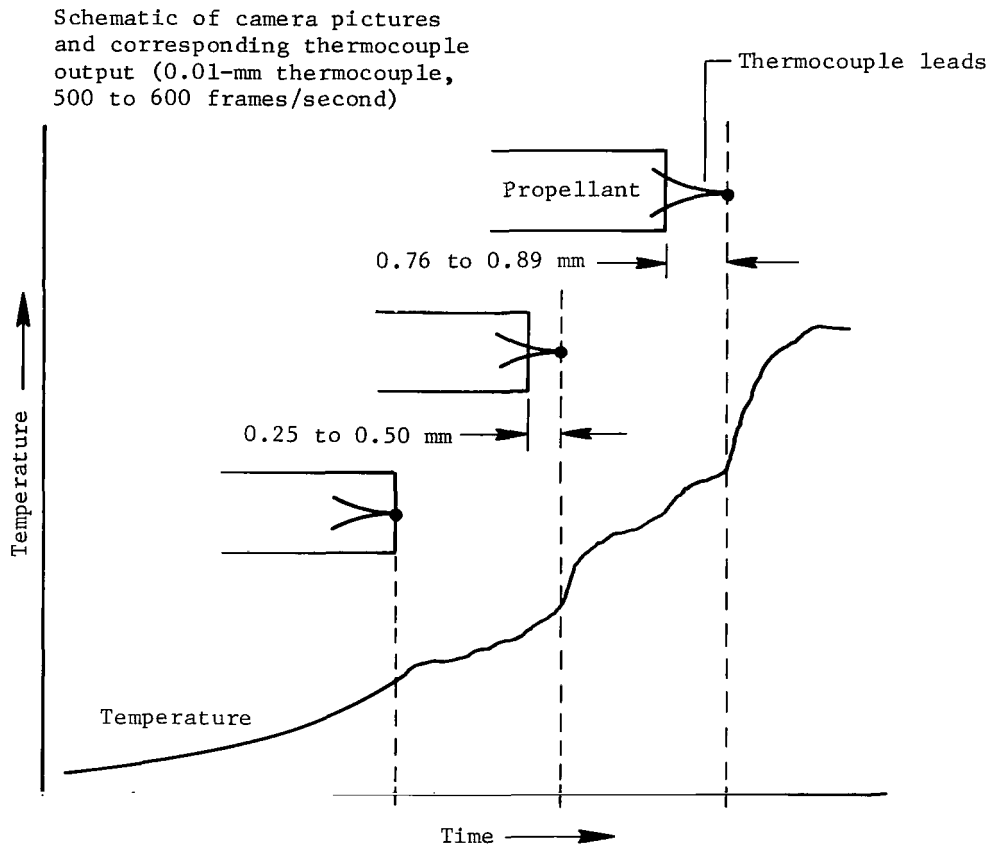


Figure 18.- Temperature jumps near surface (ref. 16).

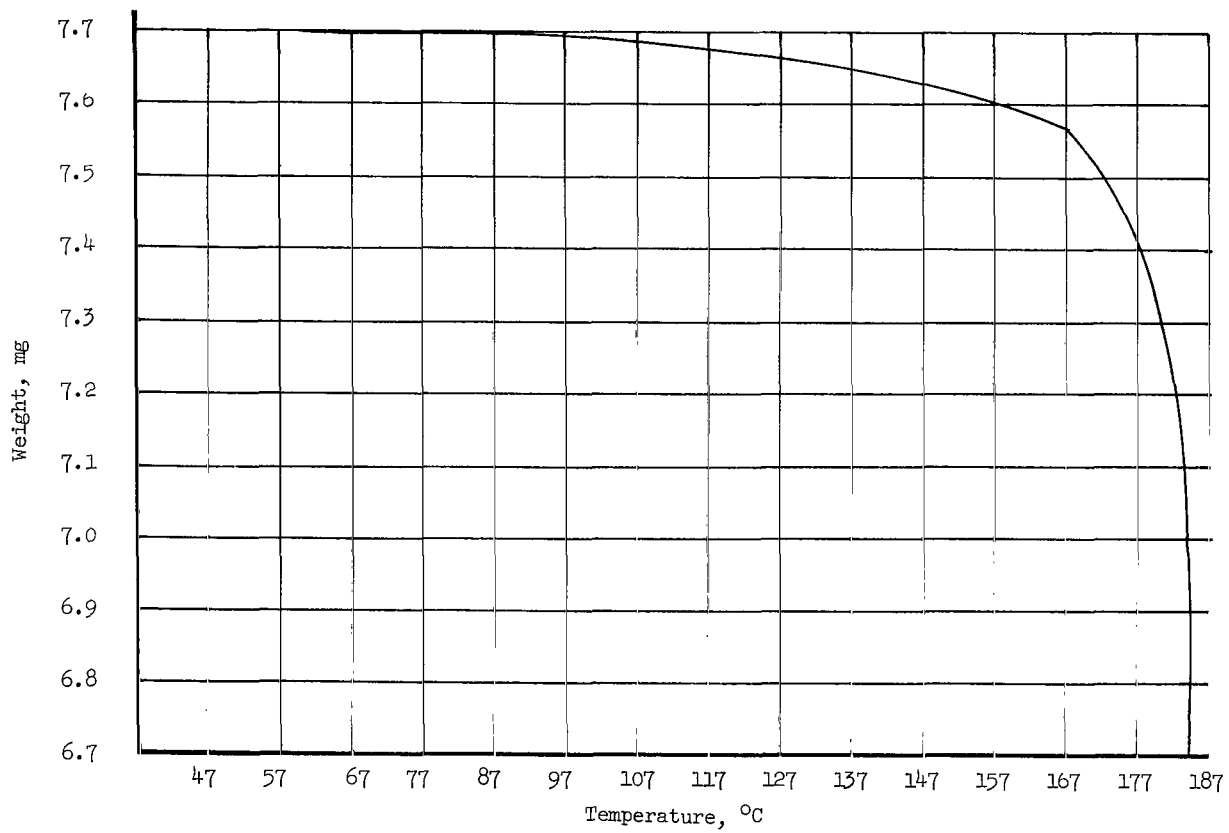


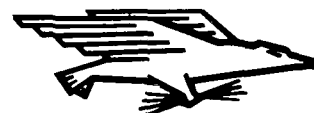
Figure 19.- TGA showing "knee" at same temperature as apparent endotherm in DSC curve. Heating rate of 10° C per minute.

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